– Supporting information –

Quantifying the Electrophilicity of a 2-Hydroxyphenyl-Substituted *para*-Quinone Methide

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Data storage system:

Folder and file names CGxxx refer to individual experiments and are identical to those in this Supporting Information.

Reactions of the enamine pyrrolidino-cyclohexene (**12**) with the two studied *p*-quinone methides are in separate folders "oHO-pQM(1b)+pyr-cyclhexene(12)" and "oTBDMSO-pQM(1a)+pyr-cyclhexene(12)".

The folders contain the following file formats:

- txt files with absorbance vs. time data [raw data]
- exp files used for the k_{obs} determination [evaluated data]
- pdf files with results of the k_{obs} determination [evaluated data].

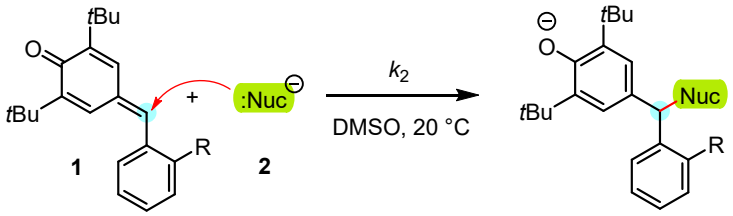
Kinetics of reactions of **1a** and **1b** with carbanions (reference nucleophiles)

Kinetic measurements were performed by harnessing UV/Vis photometry on AppliedPhotophysics SX.20 stopped-flow instruments. The kinetic measurements were initiated by mixing equal volumes of DMSO solutions of the nucleophiles and electrophiles. The temperature (20.0 ± 0.2 °C) was maintained constant by using circulating bath cryostats.

Slow reactions (**1a** + **12**, **1b** + **2b**, and **1b** + **12**) were carried out in carefully dried Schlenk glassware. The kinetics were then followed by using conventional photometric equipment, that is, a J&M TIDAS diode array spectrophotometer, which was controlled by TIDASDAQ3 (v3) software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (light path d = 5 mm) via fiber optic cables and standard SMA connectors.

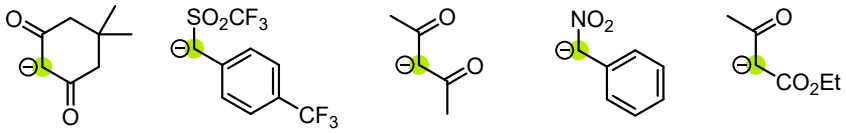
All solutions were prepared by using dry DMSO (ThermoScientific, DMSO 99.7+%, extra dry, over molecular sieve, AcroSeal) or freshly distilled acetonitrile and kept under an atmosphere of dry nitrogen. The kinetic measurements for each *p*QM/nucleophile combination were performed with or without added 18-crown-6 ether (18-c-6) for **2a**–**2h**.

Nucleophile concentrations were at least ten times higher than electrophile concentrations to achieve pseudo-first order kinetics. The first-order rate constants k_{obs} (s^{-1}) were obtained from the decay of the absorbance at or close to the absorption maximum of the reaction partner used in lower concentration by least squares fitting of the equation $A_t = A_0 \exp(-k_{obs}t) + C$ to the exponential absorption decay curve. Plots of k_{obs} (s^{-1}) versus the nucleophile concentration gave the second-order rate constants k_2 (M^{-1} s^{-1}) as slopes of the linear correlations.

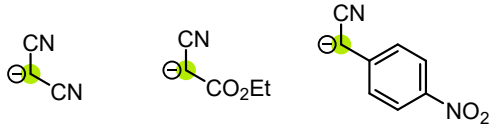


1a (R = OTBDMS)
1b (R = OH)

Reference nucleophiles:

:Nuc = 

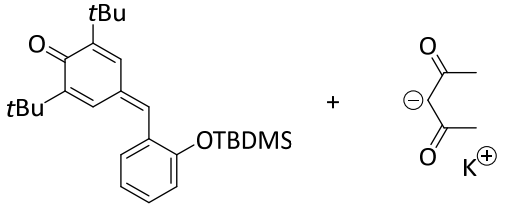
	2a	**2b**	**2c**	**2d**	**2e**
N/s_N =	16.27/0.77	17.33/0.74	17.64/0.73	18.29/0.71	18.82/0.69



2f	**2g**	**2h**	**2i**	**2j**
19.36/0.67	19.62/0.67	19.67/0.68	20.22/0.65	21.54/0.62

counterion for **2a**–**2j**: K^+

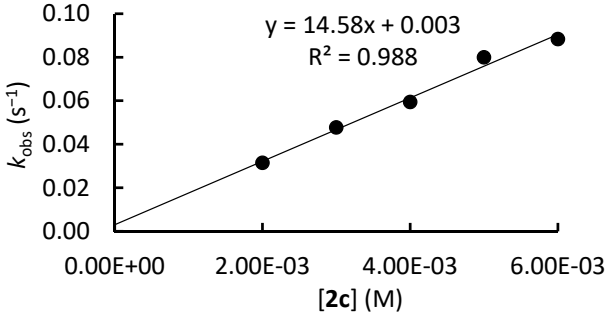
1a + **2c** in DMSO (stopped-flow method, decay at 373 nm) CG599



1a **2c**

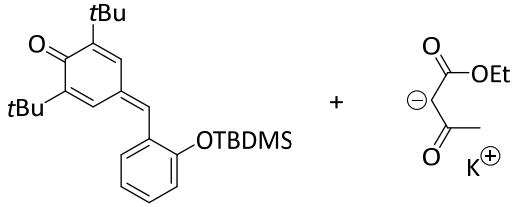
[**1a**]$_0$ (M)	[**2c**]$_0$ (M)[a]	[18-c-6]$_0$ (M)	k_{obs} (s^{-1})
2.36×10^{-5}	2.00×10^{-3}		3.15×10^{-2}
2.36×10^{-5}	3.00×10^{-3}	3.30×10^{-3}	4.77×10^{-2}
2.36×10^{-5}	4.00×10^{-3}		5.94×10^{-2}
2.36×10^{-5}	5.00×10^{-3}	5.50×10^{-3}	7.99×10^{-2}
2.36×10^{-5}	6.00×10^{-3}		8.83×10^{-2}

[a] Additionally, the reaction mixtures contained an equimolar amount of the corresponding CH-acid.



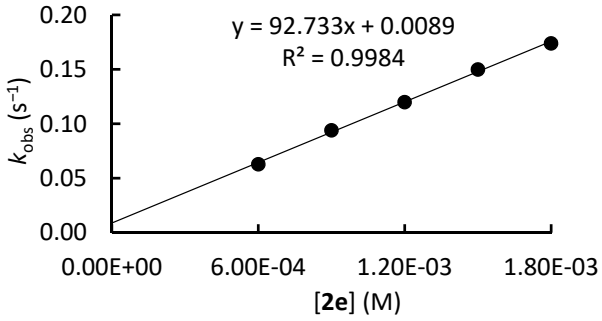
k_2 = **(1.46 ± 0.10) × 10^1 M^{-1} s^{-1}**

1a + **2e** in DMSO (stopped-flow method, decay at 373 nm) CG598



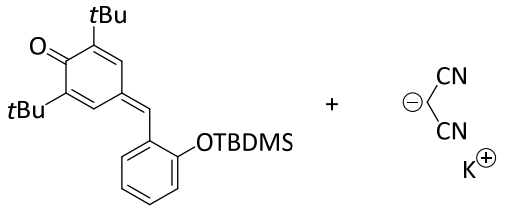
1a **2e**

[**1a**]$_0$ (M)	[**2e**]$_0$ (M)	[18-c-6]$_0$ (M)	k_{obs} (s^{-1})
2.12×10^{-5}	6.00×10^{-4}		6.29×10^{-2}
2.12×10^{-5}	9.00×10^{-4}	9.90×10^{-4}	9.40×10^{-2}
2.12×10^{-5}	1.20×10^{-3}		1.20×10^{-1}
2.12×10^{-5}	1.50×10^{-3}	1.65×10^{-3}	1.50×10^{-1}
2.12×10^{-5}	1.80×10^{-3}		1.74×10^{-1}



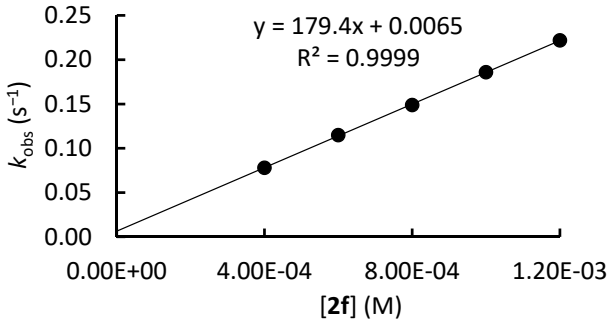
k_2 = **(9.27 ± 0.22) × 10^1 M^{-1} s^{-1}**

1a + **2f** in DMSO (stopped-flow method, decay at 373 nm) CG596



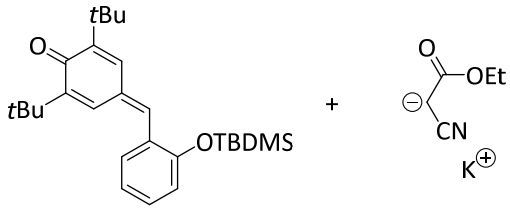
1a **2f**

$[\mathbf{1a}]_0$ (M)	$[\mathbf{2f}]_0$ (M)	$[18\text{-c-}6]_0$ (M)	k_{obs} (s^{-1})
2.08×10^{-5}	4.00×10^{-4}		7.81×10^{-2}
2.08×10^{-5}	6.00×10^{-4}	6.60×10^{-4}	1.15×10^{-1}
2.08×10^{-5}	8.00×10^{-3}		1.49×10^{-1}
2.08×10^{-5}	1.00×10^{-3}	1.10×10^{-3}	1.86×10^{-1}
2.08×10^{-5}	1.20×10^{-3}		2.22×10^{-1}



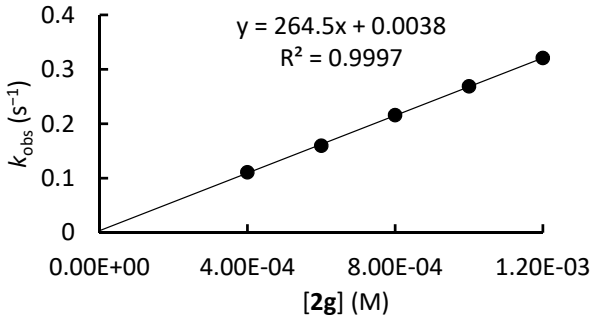
$k_2 = (1.79 \pm 0.01) \times 10^2\ M^{-1}\ s^{-1}$

1a + **2g** in DMSO (stopped-flow method, decay at 373 nm) CG597



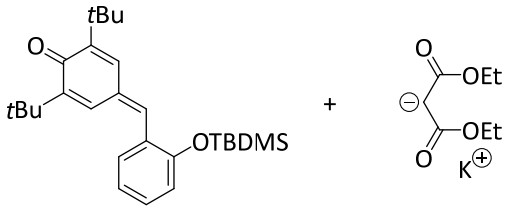
1a **2g**

$[\mathbf{1a}]_0$ (M)	$[\mathbf{2g}]_0$ (M)	$[18\text{-c-}6]_0$ (M)	k_{obs} (s^{-1})
2.03×10^{-5}	4.00×10^{-4}		1.11×10^{-1}
2.03×10^{-5}	6.00×10^{-4}	6.60×10^{-4}	1.60×10^{-1}
2.03×10^{-5}	8.00×10^{-3}		2.16×10^{-1}
2.03×10^{-5}	1.00×10^{-3}	1.10×10^{-3}	2.69×10^{-1}
2.03×10^{-5}	1.20×10^{-3}		3.21×10^{-1}



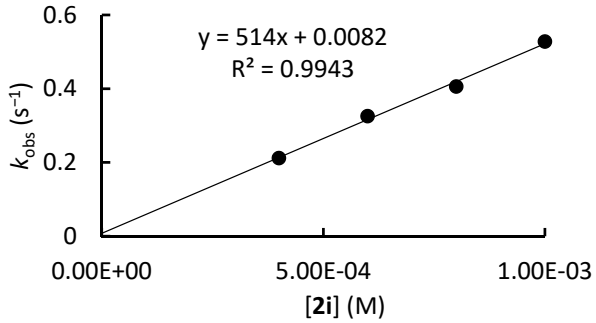
$k_2 = (2.65 \pm 0.03) \times 10^2\ M^{-1}\ s^{-1}$

1a + **2i** in DMSO (stopped-flow method, decay at 373 nm) CG595



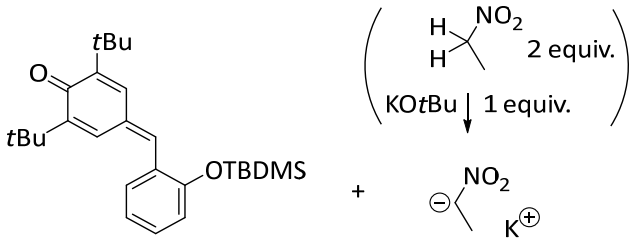
1a **2i**

$[\mathbf{1a}]_0$ (M)	$[\mathbf{2i}]_0$ (M)	$[18\text{-c-}6]_0$ (M)	k_{obs} (s^{-1})
1.98×10^{-5}	4.00×10^{-4}		2.12×10^{-1}
1.98×10^{-5}	6.00×10^{-4}	6.60×10^{-4}	3.26×10^{-1}
1.98×10^{-5}	8.00×10^{-3}		4.06×10^{-1}
1.98×10^{-5}	1.00×10^{-3}	1.10×10^{-3}	5.28×10^{-1}



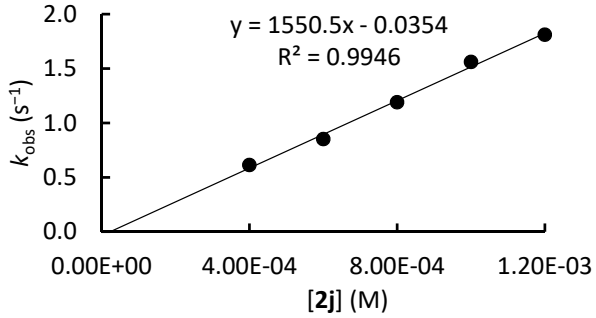
$k_2 = (5.14 \pm 0.28) \times 10^2$ M^{-1} s^{-1}

1a + **2j** in DMSO (stopped-flow method, decay at 373 nm) CG600



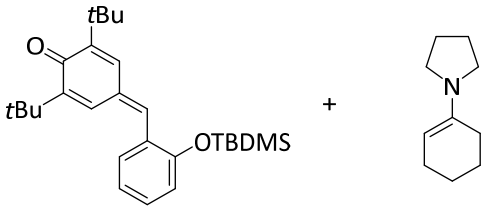
1a **2j**

$[\mathbf{1a}]_0$ (M)	$[\mathbf{2j}]_0$ (M)	$[18\text{-c-}6]_0$ (M)	k_{obs} (s^{-1})
2.36×10^{-5}	4.00×10^{-4}		6.14×10^{-1}
2.36×10^{-5}	6.00×10^{-4}	6.60×10^{-4}	8.51×10^{-1}
2.36×10^{-5}	8.00×10^{-4}		1.19
2.36×10^{-5}	1.00×10^{-3}	1.10×10^{-3}	1.56
2.36×10^{-5}	1.20×10^{-3}		1.81



$k_2 = (1.55 \pm 0.07) \times 10^3$ M^{-1} s^{-1}

1a + **12** in MeCN (conventional photometry, decay at 365 nm)

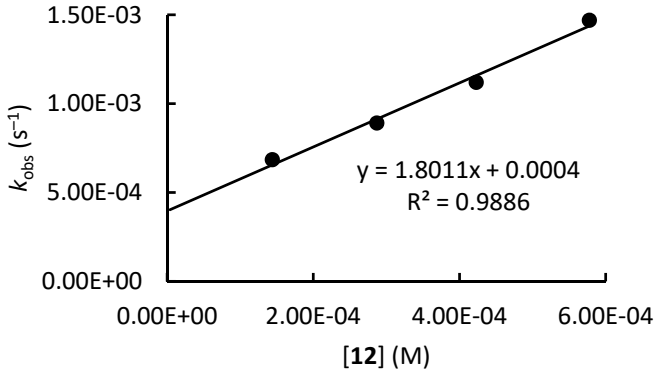


1a

+

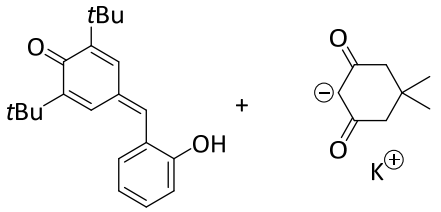
12

[**1a**]$_0$ (M)	[**12**]$_0$ (M)	k_{obs} (s^{-1})
1.94×10^{-5}	1.44×10^{-4}	6.85×10^{-4}
1.99×10^{-5}	2.87×10^{-4}	8.91×10^{-4}
1.42×10^{-5}	4.23×10^{-4}	1.12×10^{-3}
1.97×10^{-5}	5.78×10^{-4}	1.47×10^{-3}



k_2 = **(1.80 ± 0.14) M^{-1} s^{-1}**

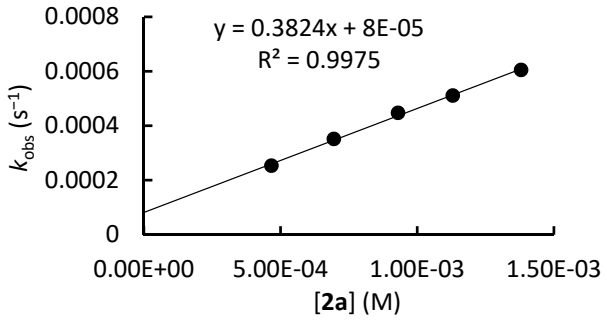
1b + **2a** in DMSO (conventional photometry, decay at 389 nm) CG604_1



1b **2a**

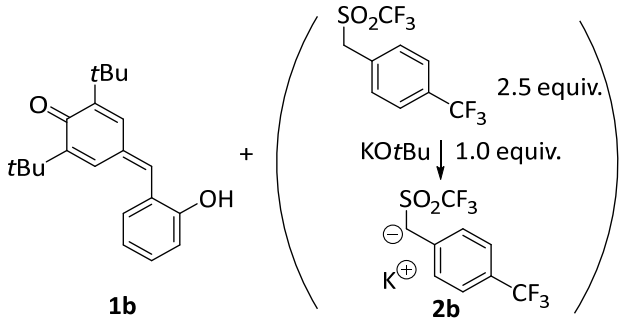
[**1b**]$_0$ (M)	[**2a**]$_0$ (M)[a]	[18-c-6]$_0$ (M)	k_{obs} (s^{-1})
4.22×10^{-5}	4.67×10^{-4}		2.53×10^{-4}
4.22×10^{-5}	6.95×10^{-4}	7.64×10^{-4}	3.51×10^{-4}
4.22×10^{-5}	9.30×10^{-4}		4.47×10^{-4}
4.22×10^{-5}	1.13×10^{-3}	1.25×10^{-3}	5.11×10^{-4}
4.22×10^{-5}	1.38×10^{-3}		6.05×10^{-4}

[a] Additionally, the reaction mixtures contained 1.4 equiv. of the corresponding CH-acid **2a**-H.



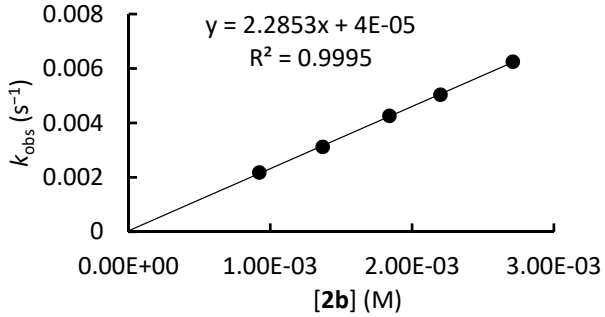
k_2 = **(3.82 ± 0.11) × 10^{-1} M^{-1} s^{-1}**

1b + **2b** in DMSO (conventional photometry, decay at 389 nm) CG603



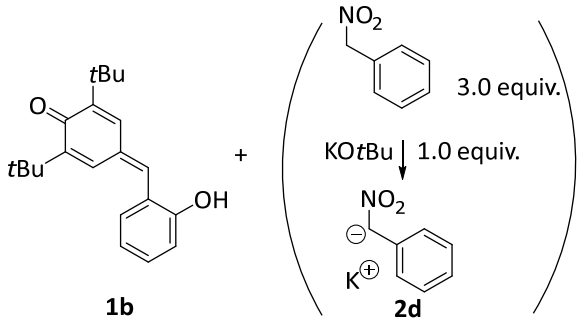
1b **2b**

[**1b**]$_0$ (M)	[**2b**]$_0$ (M)	[18-c-6]$_0$ (M)	k_{obs} (s^{-1})
8.18×10^{-5}	9.23×10^{-4}		2.18×10^{-3}
8.18×10^{-5}	1.37×10^{-3}	1.50×10^{-3}	3.12×10^{-3}
8.18×10^{-5}	1.84×10^{-3}		4.26×10^{-3}
8.18×10^{-5}	2.20×10^{-3}	2.42×10^{-3}	5.04×10^{-3}
8.18×10^{-5}	2.71×10^{-3}		6.25×10^{-3}



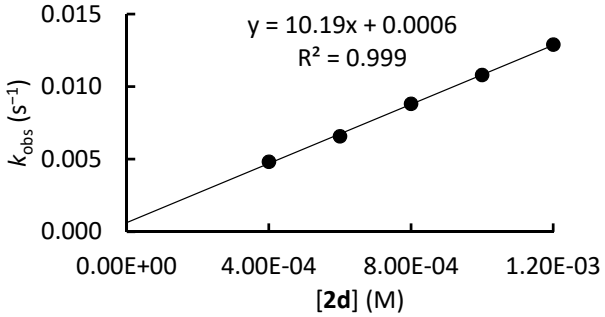
k_2 = **(2.29 ± 0.03) M^{-1} s^{-1}**

1b + **2d** in DMSO (stopped-flow method, decay at 400 nm) CG606_1



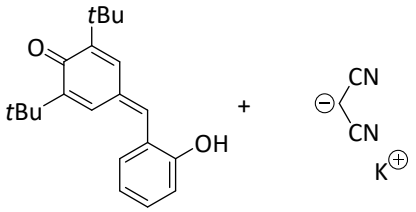
1b **2d**

[**1b**]$_0$ (M)	[**2d**]$_0$ (M)	[18-c-6]$_0$ (M)	k_{obs} (s^{-1})
1.82×10^{-5}	4.00×10^{-4}		4.82×10^{-3}
1.82×10^{-5}	6.00×10^{-4}	6.60×10^{-4}	6.58×10^{-3}
1.82×10^{-5}	8.00×10^{-4}		8.82×10^{-3}
1.82×10^{-5}	1.00×10^{-3}	1.10×10^{-3}	1.08×10^{-2}
1.82×10^{-5}	1.20×10^{-3}		1.29×10^{-2}



$k_2 = (1.02 \pm 0.02) \times 10^1\ M^{-1}\ s^{-1}$

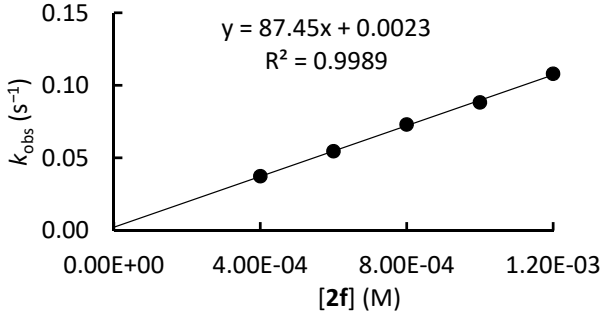
1b+ **2f** in DMSO (stopped-flow method, decay at 389 nm) CG601_1



1b **2f**

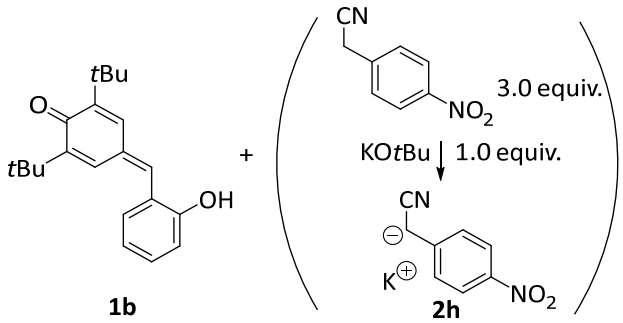
[**1b**]$_0$ (M)	[**2f**]$_0$ (M)[a]	[18-c-6]$_0$ (M)	k_{obs} (s^{-1})
2.18×10^{-5}	4.00×10^{-4}		3.74×10^{-2}
2.18×10^{-5}	6.00×10^{-4}	6.60×10^{-4}	5.46×10^{-2}
2.18×10^{-5}	8.00×10^{-3}		7.31×10^{-2}
2.18×10^{-5}	1.00×10^{-3}	1.10×10^{-3}	8.83×10^{-2}
2.18×10^{-5}	1.20×10^{-3}		1.08×10^{-1}

[a] Additionally, the reaction mixtures contained an equimolar amount of the corresponding CH-acid.



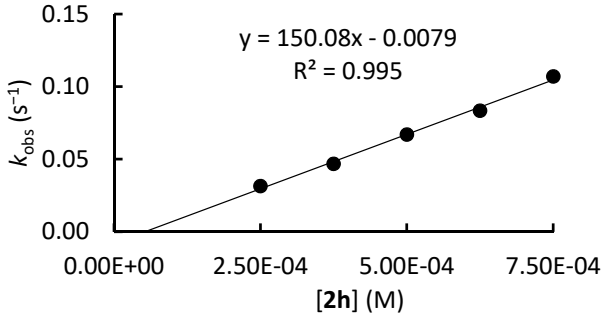
$k_2 = (8.75 \pm 0.17) \times 10^1\ M^{-1}\ s^{-1}$

1b + **2h** in DMSO (stopped-flow method, detection at 389 nm) CG602



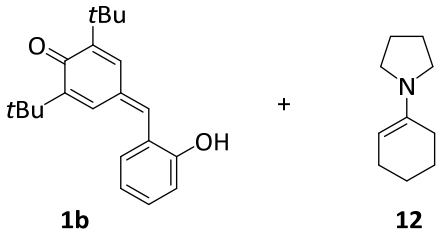
1b **2h**

[**1b**]$_0$ (M)	[**2h**]$_0$ (M)	[18-c-6]$_0$ (M)	k_{obs} (s^{-1})
2.50×10^{-5}	2.50×10^{-4}		3.15×10^{-2}
2.50×10^{-5}	3.75×10^{-4}	4.13×10^{-4}	4.68×10^{-2}
2.50×10^{-5}	5.00×10^{-4}		6.70×10^{-2}
2.50×10^{-5}	6.25×10^{-4}	6.88×10^{-4}	8.34×10^{-2}
2.50×10^{-5}	7.50×10^{-4}		1.07×10^{-1}



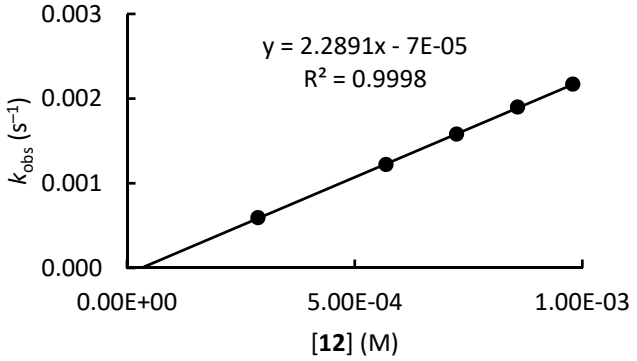
k_2 = **(1.50 ± 0.06) × 10^2 M^{-1} s^{-1}**

1b + **12** in MeCN (conventional photometry, decay at 400 nm)



1b **12**

[**1b**]$_0$ (M)	[**12**]$_0$ (M)	k_{obs} (s^{-1})
2.58×10^{-5}	2.88×10^{-4}	5.94×10^{-4}
2.54×10^{-5}	5.69×10^{-4}	1.22×10^{-3}
2.59×10^{-5}	7.24×10^{-4}	1.58×10^{-3}
2.55×10^{-5}	8.58×10^{-4}	1.90×10^{-3}
2.50×10^{-5}	9.79×10^{-4}	2.17×10^{-3}



k_2 = **(2.29 ± 0.02) M^{-1} s^{-1}**